Transit Met Chem
DOI 10.1007/s11243-016-0077-9

Synthesis and characterization of a magnetically recoverable molybdenum(VI) nanocatalyst for eco-friendly oxidation of alcohols

S. Saeednia[1] · **M. Hatefi Ardakani**[1] · **Z. Pakdin Parizi**[2] · **M. Tavakoli Hafshejani**[1]

Received: 7 April 2016 / Accepted: 23 June 2016

Abstract A catalyst based on immobilization of a molybdenum(VI) Schiff base complex on γ-Fe_2O_3 magnetic nanoparticles has been synthesized and characterized. This catalyst was employed for the selective oxidation of alcohols to the corresponding carbonyl compounds in EtOH/H_2O_2. The catalyst can be easily separated from the reaction mixture by decantation using an external magnet and reused efficiently in five subsequent reaction cycles without any significant decrease in activity or selectivity.

Introduction

One of the most fundamental organic transformations is the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds [1, 2]. Oxidizing agents such as hypervalent iodine reagents [3, 4], Cr(VI) salts [5–9] and organic-based oxidants, such as the Dess-Martin [3] and Swern [10] reagents, that are traditionally used for these oxidations are often hazardous and can produce heavy metal waste. Consequently, to overcome these shortcomings, a substantial amount of research has been directed toward the development of new and efficient catalytic systems based on the use of aqueous 30 % H_2O_2 as a final green oxidant. The advantages of H_2O_2 include low cost, environmental safety, high atom economy and water as a byproduct [11–14]. Transition metal–catalyzed oxidation of organic substrates is of current interest [6, 15–18]. In particular, molybdenum(VI) complexes can act in a similar way to molybdoenzymes and catalyze a variety of oxidation reactions [19–22]. Various molybdenum complexes are very active homogeneous and heterogeneous catalysts for oxidation–epoxidation reactions [23, 24]. Although the oxidation of alcohols can be accomplished by these methods, most of the existing protocols suffer from limitations such as low yields, long reaction times, use of organic solvents or unrecyclable catalysts and tedious work-up procedures leading to toxic waste. Recently, magnetic nanoparticles (MNPs) have received increasing interest as supporting materials for the synthesis of heterogeneous catalysts [25–28]. The advantages of MNPs include easy preparation and functionalization, large surface area-to-volume ratios, low toxicity and price [29–31]. A catalyst supported on magnetic nanoparticles can be easily separated from the reaction mixture by an external magnet and so techniques such as filtration or centrifugation are not required for catalyst recovery and recycling.

In this work, we report the synthesis, characterization and performance of a new molybdenum(VI) Schiff base complex anchored on γ-Fe_2O_3 magnetic nanoparticles as an efficient, highly recyclable and heterogeneous catalyst for the oxidation of alcohols using H_2O_2 and EtOH as a green oxidizing agent and solvent. The catalyst can be easily and completely separated from the reaction mixture by employing an external magnetic field.

Experimental

Chemicals were purchased from Merck. [$MoO_2(acac)_2$] was prepared according to the method reported in the literature [32]. The purities of the products and the progress of the reactions were monitored by TLC on silica-gel polygram

---

✉ S. Saeednia
sami_saeednia@yahoo.com; s.saeednia@vru.ac.ir

[1] Department of Chemistry, Faculty of Science, Vali-e-Asr University of Rafsanjan, Rafsanjan 77188-97111, Iran

[2] Department of Nuclear Medicine and Molecular Imaging, Razavi Hospital, Mashhad 9198613676, Iran

SILG/UV254 plates. TEM analysis was performed using a TEM microscope (Philips CM30). FTIR spectra were recorded in the 4000–400 cm^{-1} region using KBr disks on a Thermo SCIENTIFIC model NICOLET iS10 spectrophotometer. Elemental analyses were obtained on a LECO CHNS-932 analyzer. Thermogravimetric analysis (TGA) was performed on a computer-controlled NETZSCH model PC Luxx 409 apparatus. Power X-ray diffraction (XRD) patterns were recorded on a Philips X'pert diffractometer with Cu Kα ($\lambda = 0.154$ nm) radiation. Room temperature magnetization isotherms were obtained using a vibrating sample magnetometer (VSM, LakeShore 7400). The content of Mo in the catalyst was determined by ICP-OES VISTA-PRO inductively coupled plasma analyzer.

Synthesis of γ-Fe_2O_3 MNPs

γ-Fe_2O_3 MNPs were synthesized by a reported procedure, involving chemical co-precipitation of ferric and ferrous ions in alkali solution with minor modifications [33, 34]. $FeCl_2 \cdot 4H_2O$ (1.99 g) and $FeCl_3.6H_2O$ (3.25 g) were dissolved in deionized water (30 mL) under an N_2 atmosphere at room temperature. A NH_4OH solution (0.6 M, 200 mL) was then added dropwise (drop rate 1 mL min^{-1}) to the stirring mixture at room temperature to give a pH of 11. The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were then separated by an external magnet and washed with deionized water until neutralized. The synthesized sample was heated at 2 °C min^{-1} up to 250 °C and then kept in a furnace at 250 °C for 3 h to give a reddish-brown powder.

Synthesis of chloro-functionalized γ-Fe_2O_3

The prepared γ-Fe_2O_3 (3.5 g) was sonicated in dry toluene (50 mL) for 30 min. 3-Chloropropyltriethoxysilane (3.5 mL) was added to the dispersed γ-Fe_2O_3 in toluene under mechanical stirring. The mixture was slowly heated to 105 °C and kept at this temperature for 48 h. The solid was separated by an external magnet, washed three times with ethanol and dried under vacuum.

Preparation of γ-Fe_2O_3–diamine

The chloro-functionalized γ-Fe_2O_3 (3.5 g) was dispersed by sonication in dry toluene (50 mL) for 30 min. 1,3-Diamino-propan-2-ol (0.4 g) was then added under mechanical stirring. The mixture was slowly heated to 105 °C and kept at this temperature for 24 h. The solid was separated by an external magnet, washed three times with ethanol and dried under vacuum.

Synthesis of Schiff base immobilized on γ-Fe_2O_3 (γ-Fe_2O_3-L)

γ-Fe_2O_3-diamine (3.5 g) was sonicated in absolute methanol (50 mL) for 30 min. Salicylaldehyde (1.5 mL) was added slowly to the mixture, which was then stirred at 65 °C for 24 h. After cooling to room temperature, the solid was separated by an external magnet, washed with methanol and dried at 60 °C under vacuum.

Preparation of molybdenum Schiff base complex immobilized on γ-Fe_2O_3 (γ-Fe_2O_3-MoO_2L)

γ-Fe_2O_3-L (3.5 g) was sonicated in dry methanol (30 mL) for 30 min. $MoO_2(acac)_2$ (1.2 g) was added to the dispersed mixture under mechanical stirring, and the mixture was refluxed for 24 h. The solid was separated by an external magnet and washed three times with methanol. It was then dried under vacuum at 60 °C overnight to furnish the corresponding γ-Fe_2O_3-supported complex.

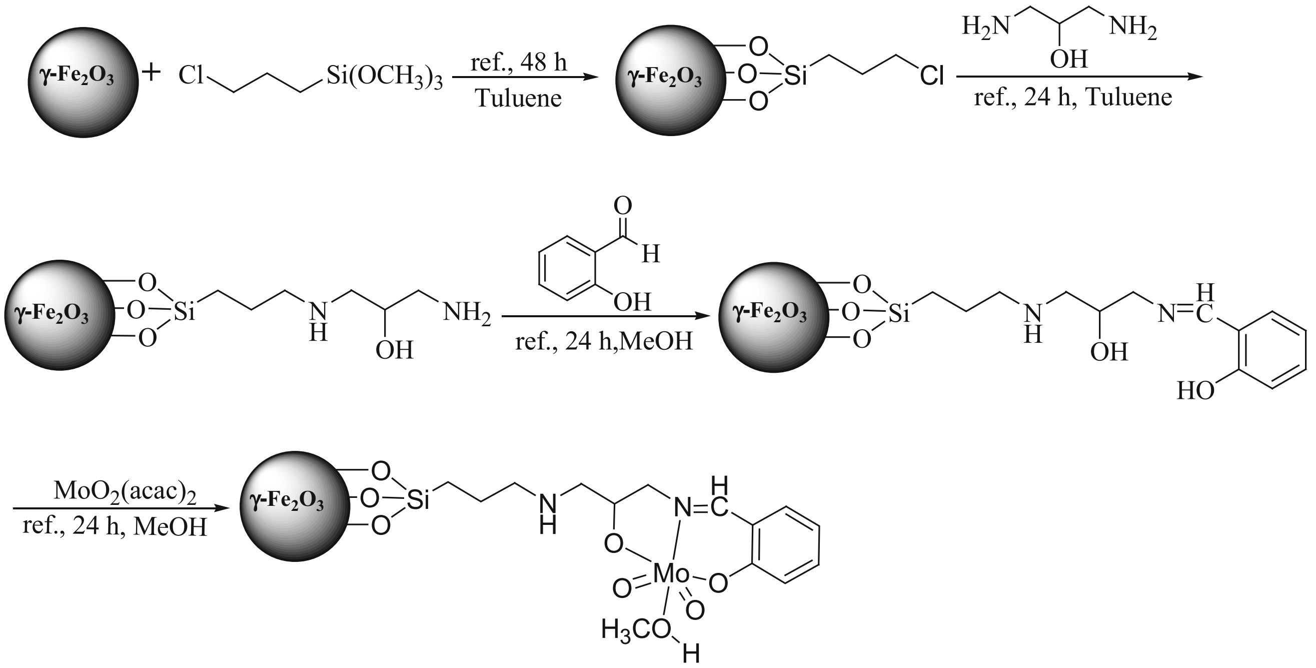
General procedure for oxidation of alcohols

Catalytic experiments were carried out in a 5-mL test tube. In a typical procedure, to 1 mmol benzyl alcohol in 1 ml solvent, 2 mol% (0.02 g) of γ-Fe_2O_3-MoO_2L and 2 mmol of 30 % H_2O_2 was added. The reaction mixture was stirred for 3 h at 80 °C. The reaction products were monitored by TLC or GC. After completion of the reaction, the mixture was diluted with EtOAc. The catalyst was separated by an external magnet, washed with EtOAc, dried and reused for a consecutive run under the same reaction conditions. Evaporation of the solvent from the filtrate under reduced pressure gave the crude products, which were then purified by chromatography on silica gel eluted with n-hexane/EtOAc (2:1).

Results and discussion

Catalyst synthesis and characterization

The synthetic procedure to obtain the catalyst is outlined in Scheme 1. First, γ-Fe_2O_3 MNPs were synthesized by chemical co-precipitation of ferric and ferrous ions from alkaline solution [33, 34]. The resulting γ-Fe_2O_3 was then functionalized with 3-chloropropyltriethoxysilane. Next, 1,3-diamino-propan-2-ol was added to obtain γ-Fe_2O_3-diamine. This reaction was followed by condensation with salicylaldehyde to give a tridentate Schiff base immobilized on γ-Fe_2O_3 (γ-Fe_2O_3-L). Finally, reaction with a



Scheme 1 Synthesis of γ-Fe$_2$O$_3$-MoO$_2$L

methanol solution of MoO$_2$(acac)$_2$ gave γ-Fe$_2$O$_3$-MoO$_2$L (Scheme 1).

The size and structure of the synthesized catalyst were evaluated using transmission electron microscopy (TEM). TEM images revealed an approximately spherical shape for γ-Fe$_2$O$_3$-MoO$_2$L with an average diameter of 15 ± 5 nm (Fig. 1).

The crystalline structures of γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$-MoO$_2$L were characterized by X-ray diffraction (XRD) (Fig. 2). The XRD pattern of γ-Fe$_2$O$_3$ showed characteristic peaks that matched with those of standard γ-Fe$_2$O$_3$ nanoparticles (JCPDS file no. 04-0755), with a unit cell dimension of 8.35 Å and space group of *P*4132 (213). The same set of peaks was observed in the XRD pattern of γ-Fe$_2$O$_3$-MoO$_2$L, indicating the stability of the crystalline nanoparticles phase during surface modification. The deduced average size of the γ-Fe$_2$O$_3$-MoO$_2$L nanoparticles from Scherrer's formula was about 15.8 nm.

Thermogravimetric analysis (TGA) was used to study the thermal stability of the catalyst. The thermal behavior of γ-Fe$_2$O$_3$-MoO$_2$L is shown in Fig. 3. A weight loss of about 8.55 wt% between 25–580 °C can be attributed to the loss of organic components attached to the surface. According to the TGA, the amount of organic components functionalized on γ-Fe$_2$O$_3$ was 0.18 mmol g^{-1}. These results were in good agreement with the elemental analysis

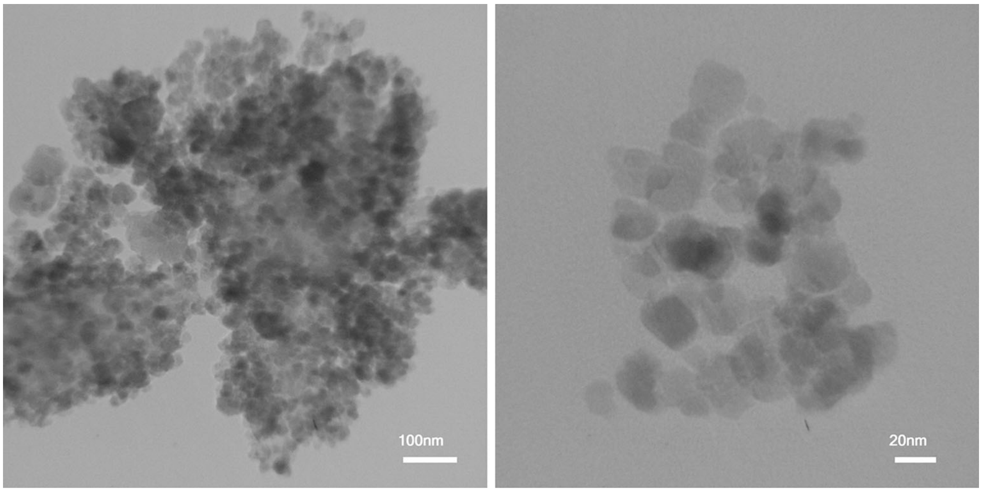


Fig. 1 TEM images of γ-Fe$_2$O$_3$-MoO$_2$L

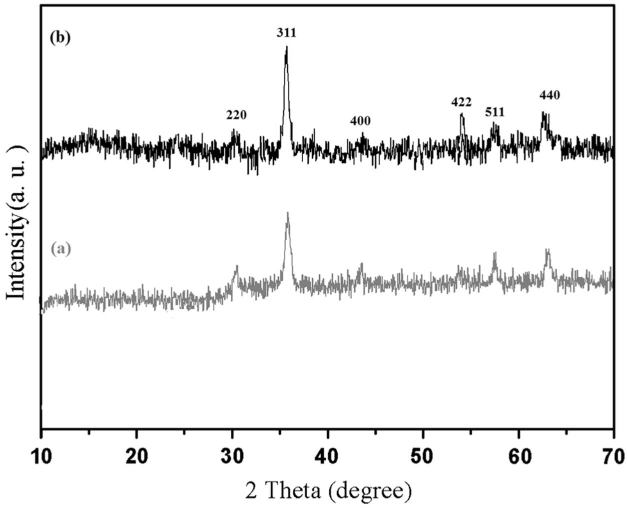


Fig. 2 XRD patterns of **a** γ-Fe_2O_3 and **b** γ-Fe_2O_3-MoO_2L

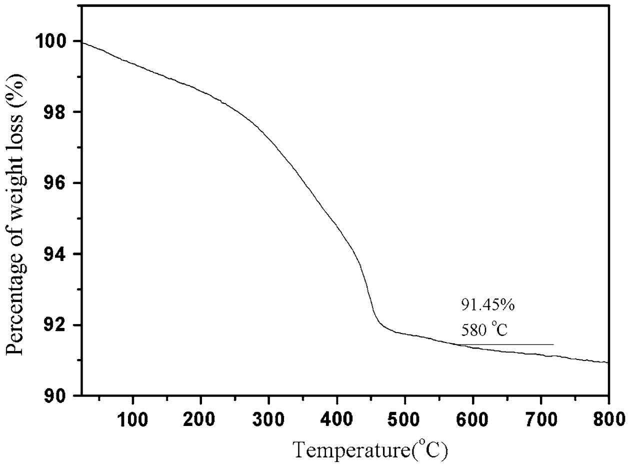


Fig. 3 TGA diagram of γ-Fe_2O_3-MoO_2L

data (N = 0.54 %) and the ICP analysis, which showed that 0.19 mmol of molybdenum was anchored on 1.0 g of γ-Fe_2O_3-MoO_2L catalyst.

The immobilization of the molybdenum Schiff base complex on γ-Fe_2O_3 was monitored by FTIR spectroscopy (Fig. 4). A band at around 550–650 cm^{-1} is assigned to the Fe–O bond stretching vibrations in γ-Fe_2O_3, while an intense band in the range of 1000–1300 cm^{-1} is assigned to the Si–O stretching bond in chlorosiloxane-functionalized γ-Fe_2O_3 (Fig. 4b). In the FTIR spectrum of the Schiff base immobilized on γ-Fe_2O_3 (Fig. 4c), a band at 1650 cm^{-1} is assigned to the C=N stretch and some weak bands at 1200–1300 cm^{-1} are assigned to the aromatic rings of the Schiff base. These features were not present in the parent γ-Fe_2O_3. After reaction of γ-Fe_2O_3-L with $MoO_2(acac)_2$, the imine stretch is shifted to 1620 cm^{-1}, Fig. 4d, indicating complexation of this group with the metal. In the FTIR spectrum of γ-Fe_2O_3-MoO_2L, two bands at 934 and 903 cm^{-1} can be assigned to the stretching vibrations of the Mo=O groups loaded onto MNPs [27]. A strong and broad band in the range of 2800–3700 cm^{-1} corresponds to the hydrogen-bonded adsorbed water, overlapped with C–H stretching vibrations of the phenyl and CH_2 groups [27]. A band at 1660 cm^{-1} in Fig. 4a, b is assigned to adsorbed water [33].

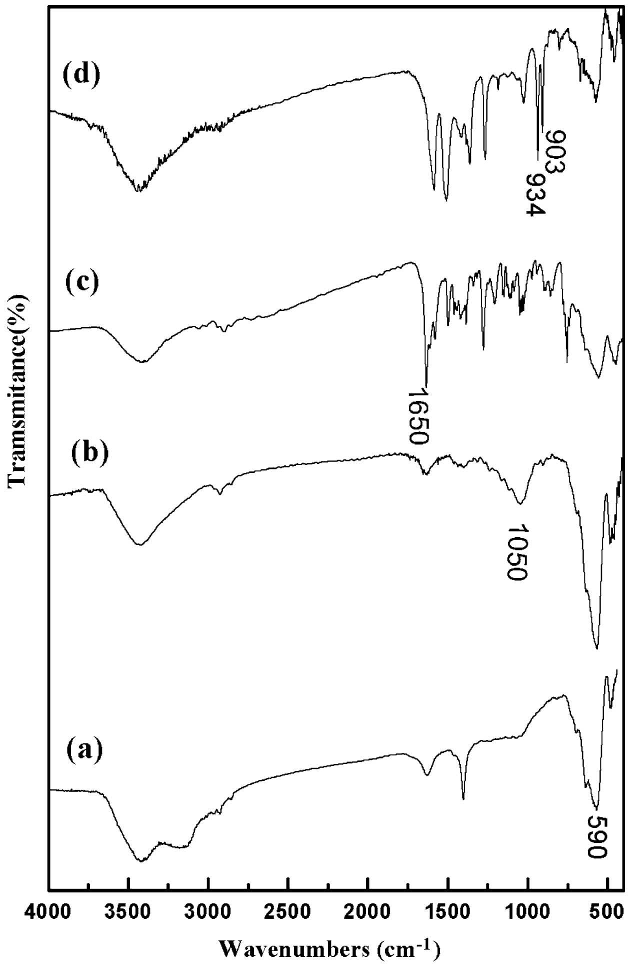


Fig. 4 FTIR spectra of **a** γ-Fe_2O_3, **b** chloro-functionalized γ-Fe_2O_3, **c** γ-Fe_2O_3-L and **d** γ-Fe_2O_3-MoO_2L

The magnetization curves of γ-Fe_2O_3 and γ-Fe_2O_3-MoO_2L were measured at room temperature with a vibrating sample magnetometer (VSM). As shown in Fig. 5, no reduced remanence and coercivity were detected, indicating both unmodified and Mo-modified γ-Fe_2O_3 are superparamagnetic. The saturation magnetic moments of γ-Fe_2O_3 and γ-Fe_2O_3-MoO_2L are 68.8 and 65.5 emu g^{-1}, respectively.

Catalytic activities of γ-Fe_2O_3-MoO_2L for the oxidation of alcohols

Following the successful synthesis and characterization of γ-Fe_2O_3-MoO_2L, its catalytic activity was studied for the

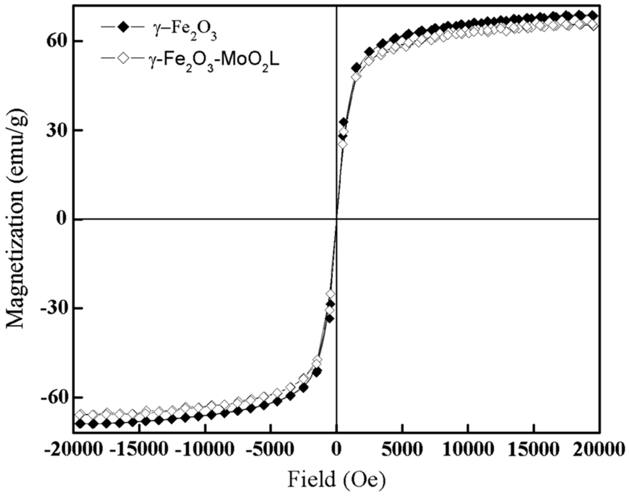


Fig. 5 Magnetization curves of γ-Fe_2O_3 and γ-Fe_2O_3-MoO_2L

oxidation of alcohols to the corresponding aldehydes or ketones with aqueous 30 % H_2O_2 as the terminal oxidant. The oxidation of benzyl alcohol (1 mmol) to benzaldehyde as a test reaction was first investigated in various solvents and at different temperatures, to find the optimum reaction conditions (Table 1). Initially, this reaction was investigated under solvent-free condition, as well as in different solvents (entries 1–10). The best yield of the desired product was obtained in ethanol at 80 °C (entry 2). A similar reaction at lower temperature required more time and produced lower yields (entriy 11). Next, the influence of different oxidants on the oxidation of benzyl alcohol in ethanol at 80 °C was studied (entries 12–14). Hydrogen peroxide proved to be the best choice among the examined oxidants (entry 2). The reaction did not proceed well in the absence of any oxidant, giving only a trace amount of the desired product (entry 15). Similarly, when 1 mmol of the oxidant was used, the yield of the desired product was decreased (entry 16). Similar reactions performed in the presence of different amounts of γ-Fe_2O_3-MoO_2L (entries 17 and 18) showed that 2 mol% of the catalyst gave the best results (entry 2). The model reaction was also examined in the presence of γ-Fe_2O_3 and $MoO_2(acac)_2$ rather than the γ-Fe_2O_3-MoO_2L catalyst (entries 19–21) and low amounts of the desired product were obtained.

In order to establish the generality of this method, the oxidation of a variety of primary and secondary alcohols under the optimized reaction conditions was investigated (Table 2). Substituted benzyl alcohols bearing either electron-releasing or withdrawing groups were also oxidized selectively and afforded the corresponding aldehydes in good to excellent yields (entries 1–6). Moreover, relatively hindered benzyl alcohols were also converted to the corresponding aldehydes in good yields without any overoxidation to the corresponding carboxylic acid under the same reaction conditions (entries 2, 3, 5). In particular, the heteroaromatic furfuryl alcohol, which is considered to be a challenging substrate in most transition metal catalyst systems, was oxidized selectively to furfural in this system (entry 7). Linear alcohols were also oxidized efficiently with H_2O_2 by this catalyst (entries 8–10), while secondary alcohols gave the corresponding ketones in good yields (entries 11–16).

In order to investigate the chemoselectivity of the system, a competitive reaction was designed. A mixture of equal amounts of benzyl alcohol and 2-phenyl ethanol was subjected to oxidation under the condition given in Table 2 (Scheme 2). In this experiment, benzyl alcohol was oxidized to benzaldehyde, but 2-phenyl ethanol was left unreacted.

Table 1 Oxidation of benzyl alcohol to benzaldehyde under different conditions

Entry	Oxidants	T (°C)	Solvent (0.5 mL)	Yield[a] (%)
1	H_2O_2	80	–	60
2	H_2O_2	80	EtOH	85
3	H_2O_2	80	Toluene	55
4	H_2O_2	60	CH_3OH	45
5	H_2O_2	55	THF	55
6	H_2O_2	60	$CHCl_3$	20
7	H_2O_2	80	CH_3CN	60
8	H_2O_2	60	CH_2Cl_2	15
9	H_2O_2	80	H_2O	60
10	H_2O_2	80	DMSO	Trace
11	H_2O_2	50	EtOH	50
12	O_2^b	80	EtOH(1 mL)	50
13	TBHP	80	EtOH	25
14	UHP	80	EtOH	70
15	–	80	EtOH	Trace
16[c]	H_2O_2	80	EtOH	60
17[d]	H_2O_2	80	EtOH	50
18[e]	H_2O_2	80	EtOH	85
19[f]	H_2O_2	80	EtOH	Trace
20[g]	H_2O_2	80	EtOH	10
21[h]	H_2O_2	80	EtOH	30

[a] Isolated yield, reaction conditions: benzyl alcohol (1 mmol), oxidant (2 mmol, except for Entries 12–16), γ-Fe_2O_3-Mo (2 mol%, except for Entries 17–21), reaction time: 3 h

[b] 60 bubble/min

[c] 1 mmol H_2O_2

[d] Catalyst: 1 mol%

[e] Catalyst: 3 mol%

[f] No catalyst

[g] Catalyst: γ-Fe_2O_3 (2 mol%)

[h] Catalyst: $MoO_2(acac)_2$ (2 mol%)

Table 2 Oxidation of alcohols with H_2O_2 catalyzed by γ-Fe_2O_3-MoO_2L

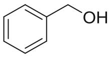
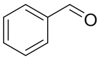
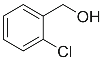
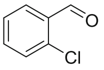
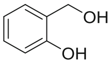
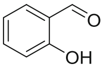
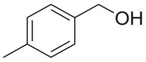
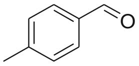
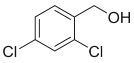
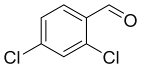
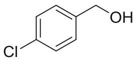
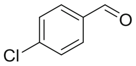
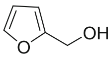
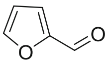
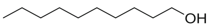
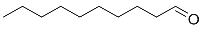
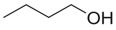
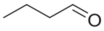
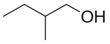
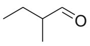
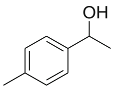
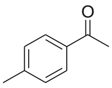
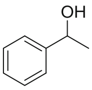
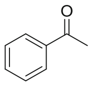
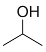
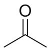
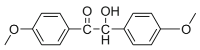
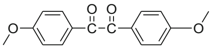
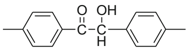
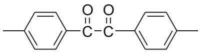
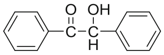
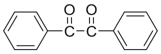
Entry	Alcohol	Product	Time(h)	Yield[a] (%)
1			3	85
2			4	70
3			3	60
4			3	85
5			3	80
6			3	85
7			4	60
8			4	60[b]
9			4	65[b]
10			3	70[b]
11			3	85
12			4	80
13			3	50[b]
14[c]			4	65

Table 2 continued

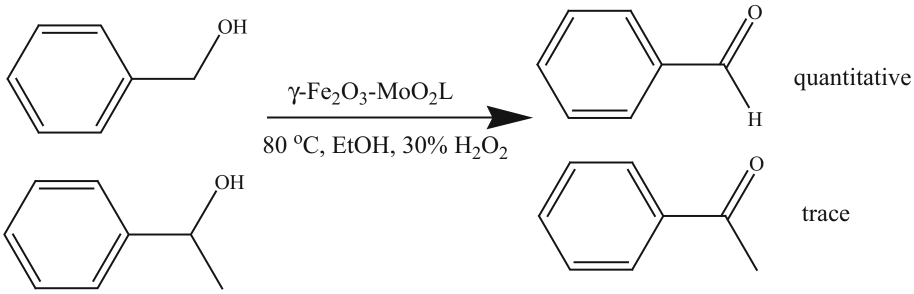
Entry	Alcohol	Product	Time(h)	Yield[a] (%)
15[c]			3	65
16[c]			3	70

[a] Isolated yield, conditions: alcohol (1 mmol), hydrogen peroxide (2 mmol), catalyst (2 mol%), temperature: 80° C

[b] Yield determined by GC analysis

[c] The alcohols were synthesized according to Ref [35]

Scheme 2 Chemoselectivity of the catalyst



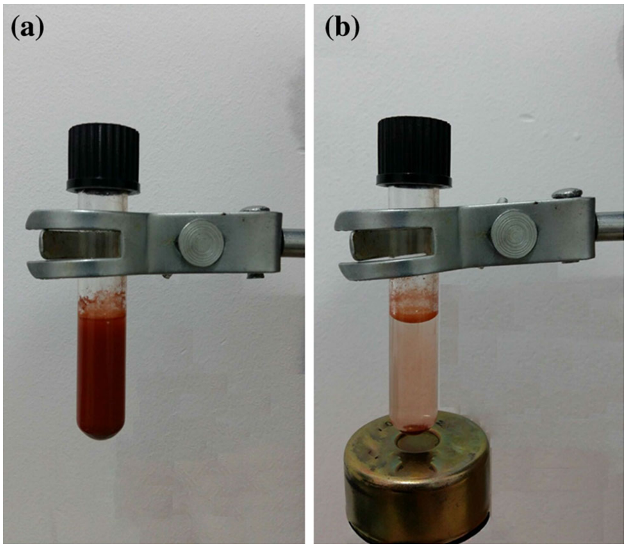


Fig. 6 **a** Reaction mixture, **b** Separation of γ-Fe_2O_3-MoO_2L from the reaction mixture by an external magnet

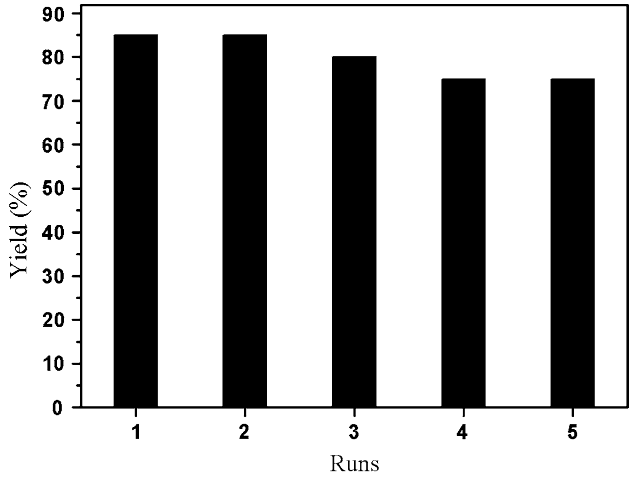


Fig. 7 Reusability of γ-Fe_2O_3-MoO_2L in selective oxidation of benzyl alcohol to the benzaldehyde with 30 % H_2O_2

The recyclability of a heterogeneous catalyst is of great importance and provides a critical advantage over homogeneous catalysts. The magnetic properties of γ-Fe_2O_3-MoO_2L facilitate efficient recovery of the catalyst from the reaction mixture. Thus, after performing the oxidation of benzyl alcohol with hydrogen peroxide, the catalyst was separated by an external magnet from the reaction mixture (Fig. 6), washed with EtOAc and dried for 30 min at 80 °C. In this way, the recycled catalyst was successfully used in at least five reaction cycles with only slight decrease in catalytic performance (Fig. 7). ICP analyses of γ-Fe_2O_3-MoO_2L after five such cycles showed that only a very small amount of Mo had been removed from the catalyst. The TEM image of used γ-Fe_2O_3-MoO_2L (Fig. 8) compared with the fresh catalyst showed that the morphology remained intact after five cycles, while the FTIR spectrum (Fig. 9) of the reused

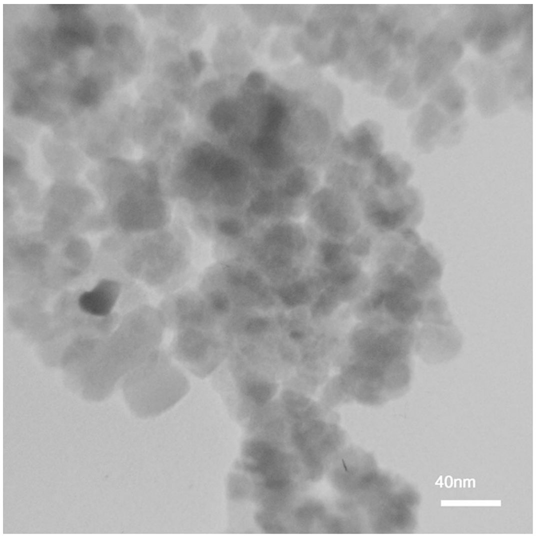


Fig. 8 TEM image after five times reuse of γ-Fe_2O_3-MoO_2L

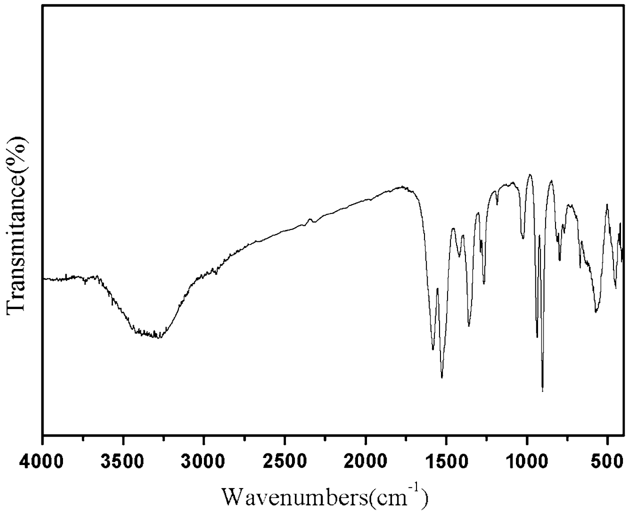


Fig. 9 FTIR spectrum of γ-Fe_2O_3-MoO_2L after five times reuse

catalyst also showed no detectable changes compared to the fresh catalyst (Fig. 4).

Conclusions

In summary, a molybdenum Schiff base complex immobilized on γ-Fe_2O_3 magnetic nanoparticles was synthesized, characterized and applied as a magnetically recyclable heterogeneous catalyst in the activation of 30 % H_2O_2 for the selective oxidation of alcohols to their corresponding carbonyl compounds. Primary aromatic and aliphatic alcohols were selectively converted to the corresponding aldehydes without over-oxidation to the corresponding carboxylic acids. Moreover, secondary alcohols were also oxidized to the corresponding ketones with good to excellent yields. The catalyst was successfully recovered from the reaction mixture and reused for five subsequent reaction cycles with only slight decrease in its activity.

Acknowledgments The support of this work by Vali-e-Asr University of Rafsanjan is acknowledged.

References

1. Hudlicky M (1990) Oxidation in organic chemistry, ACS monograph series. American Chemical Scociety, Washington DC
2. Sheldon RA, Kochi JK (1984) Metal catalyzed oxidations of organic compounds. Academic Press, New York
3. Dess DB, Martin JC (1983) J Org Chem 48:4155
4. Dess DB, Martin JC (1991) J Am Chem Soc 113:7277
5. Cainelli G, Cardillo G (1984) Chromium oxidation in organic chemistry. Springer, Berlin
6. Matsumoto T, Ueno M, Wang N, Kobayashi S (2008) Chem Asian J 3:196
7. Mallat T, Baiker A (2004) Chem Rev 104:3037
8. Jamwal N, Gupta M, Paul S (2008) Green Chem 10:999
9. Hackett SFJ, Brydson RM, Gass MH, Harvey I, Newman AD, Wilson K, Lee AF (2007) Angew Chem Int Ed 46:8593
10. Mancuso AJ, Huang S-L, Swern D (1978) J Org Chem 43:2480
11. Biradar AV, Dongare MK, Umbarkar SB (2009) Tetrahedron Lett 50:2885
12. Jones CW (1999) Applications of hydrogen peroxide and derivatives, vol. 2. (Royal Society of Chemistry, 1999)
13. Centi G, Fabrizio C, Ferrucio T (2012) Selective oxidation by heterogeneous catalysis. Springer Science & Business Media
14. Maggi R, Chitsaz S, Loebbecke S, Piscopo CG, Sartori G, Schwarzer M (2011) Green Chem 13:1121
15. Vinod CP, Wilson K, Lee AF (2011) J Chem Technol Biotechnol 86:161
16. Ciriminna R, Pagliaro M (2010) Org Process Res Dev 14:245
17. Piera J, Bäckvall J-E (2008) Angew Chem 120:3558
18. Piera J, Bäckvall J-E (2008) Angew Chem Int Ed 47:3506
19. Khanbabaee KK (1993) Ann Chem 905
20. Wang W, Daran JC, Poli R, Agustin D (2016) J Mol Catal A: Chem 416:117
21. Ghorbanloo M, Mohamadi A, Amini M (2015) J Tao Transit Metal Chem 40:321
22. Tadayonpour N, Rayati S, Sadr MH, Zare K, Wojtczak A (2015) Transit Metal Chem 40:891
23. Manyar HG, Chaure GS, Kumar A (2006) J Mol Catal A 243:244
24. Zhang J, Jiang P, Shen Y, Zhang W, Li X (2015) Microporous Mesoporous Mater 206:161
25. Masteri-Farahani M, Kashef Z (2012) J Magn Magn Mater 324:1431
26. Rafiee E, Evani S (2011) Green Chem 13:2116
27. Zare M, Moradi-Shoeili Z, Bagherzadeh M, Akbayrak S, Özkar S (2016) New J Chem 40:1580
28. Rayati S, Abdolalian P (2013) C R Chim 16:814
29. Abu-Reziq R, Wang D, Post M, Alper H (2008) Chem Mater 20:2544
30. Keypour H, Balali M, Haghdoost MM, Bagherzadeh M (2015) RSC Adv. 5:53349
31. Bezaatpour A, Khatami S, Amiri M (2016) RSC Adv. 6:27452
32. Chen GJJ, McDonald JW, Newton WE (1976) Inorg Chem 15:2612
33. Sobhani S, Pakdin-Parizi Z (2014) RSC Adv. 4:13071
34. Ho KM, Li P (2008) Langmuir 24:1801
35. Mavis ME, Yolacan C, Aydogan F (2010) Tetrahedron Lett 51:4509